

¹A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS

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ABSTRACT

A

Tough, slightly flexible polymers were made by the reaction of p, p'-biphenol with methylphenyl silylamines. One polymer with a molecular weight of 150,000 was soluble in tetrahydrofuran, and it apparently has some merit as an adhesive. The shear strength in lap joints with either aluminum or stainless steel was 4,000-5,000 psi. The polymers had good thermal stability, but they softened in the range of 100-200°C.

The reaction of hexaphenylcyclotrisilazane with ethylene glycol produced a soft elastomer with a slow recovery time. The elastomer had a low melting point, but it could be cured in air to a solid coating that endured 400°C for 17 hours.

Aluminum ethoxide catalyzed a polymerization reaction between diphenyldiethoxysilane and bis(methylamino)diphenylsilane, but the products were brittle with no apparent utility.

Attempts were made to improve ethylenediamine silazane by reactions with ethylene oxide and bis(methylamino)diphenylsilane, but the improvements in properties for coatings were too small to be significant.

Additional work on the silicon-nitrogen polymers with phenylene bridges has not produced polymers as strong as those initially produced. Molecular weight seems to be part of the problem.

A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

I. INTRODUCTION AND STATUS

Silicon-nitrogen compounds are being studied in an effort to produce thermally stable materials that will be useful in the space program. This report covers the tenth month of the fourth year of the project.

The most promising of the types of polymers presently being investigated are one containing -Si-N-Si- units jointed by phenylene units and one containing -O-Si-O- joined by various aromatic units. The reaction to produce the latter type was first studied at the George C. Marshall Space Flight Center.

Several other reactions are being studied as possible routes to silicon-nitrogen polymers. Aluminum ethoxide reacts with silicon-nitrogen compounds, but the polymers produced have all been brittle and they continued to react at high temperatures with resulting degradation.

Attempts are being made to improve the stable but weak elastomers made with ethylenediamine silazane. A treatment of ethylenediamine silazane with bis(methylamino)diphenylsilane resulted in a small improvement in the toughness of coatings made from the product, but the improvement was not enough to make the product of interest for coatings if used alone.

Work is being continued on the silicon-nitrogen polymers with phenylene bridges to produce additional quantities of the tough stable elastomer that was made formerly. More intense efforts to purify the reactants seems to have resulted in less strength.

II. REACTIONS OF SILYLAMINES WITH DIHYDROXY COMPOUNDS

A. Discussion

The reaction of silylamines with dihydroxy compounds to produce polymers was studied further by treating hexaphenylcyclotrisilazane with ethylene glycol and by treating the methylphenyl methylamino silazane with p, p'-biphenol.

Ethylene glycol reacted readily with hexaphenylcyclotrisilazane at 175-225°C to produce a soft elastic polymer with excellent elongation but low tensile strength and slow recovery time. It broke readily when the rate of elongation was rapid, but it could be stretched to a thin film if pulled slowly. The elastomer was soluble in benzene, and it had moderately good stability as a coating. After being heated on an aluminum panel at 400°C for 17 hours or 500°C for 1 hour, it protected the aluminum from hydrochloric acid except where the panel had been bent.

The methylphenyl methylamino silazane reacted readily with p, p'-biphenol to form tough polymers. One preparation had a molecular weight of 150,000 and was soluble in tetrahydrofuran. This sample was molded into a disc about 3 cm in diameter and 2 mm thick. The disc was rigid at room temperature and elastic at 100°C. As an adhesive for either aluminum or stainless steel, the polymer had a shear strength of 4000-5000 psi in a single lap joint. The polymer had good thermal stability, but it was quite soft at 200°C. The low softening point will doubtless restrict its utility.

The methylphenyl anilino silazane also reacted readily with p, p'-biphenol. Long fibers could be drawn from the resulting melt, but they had little or no strength at 100°C.

B. Experimental Details

1. Reaction of hexaphenylcyclotrisilazane and ethylene glycol

Two reactions were run with hexaphenylcyclotrisilazane and ethylene glycol—one with triethylamine present and one without. The amine did not aid polymerization.

a. Reaction of hexaphenylcyclotrisilazane and ethylene glycol with triethylamine present initially

In a 50-ml, 3-neck round-bottom flask, equipped with a magnetic stirrer, thermometer, dropping funnel, and reflux condenser were placed 5.0 g (0.0084 moles) of hexaphenylcyclotrisilazane and 20.0 g (27.8 ml, 0.198 mole) of purified triethylamine. Then 1.39 ml (1.56 g, 0.0252 mole) of recently distilled ethylene glycol in 7.2 g (10.0 ml, 0.071 mole) of triethylamine was dropped with stirring into the reaction flask. When no rise in temperature occurred, heat was applied and the mixture was stirred at 50-60°C for 1.0 hr. The heat input was then increased, and the mixture was refluxed at 90°C for 1.0 hr. At the end of this time, the hexaphenylcyclotrisilazane had not gone into solution and did not appear to have reacted. The triethylamine was distilled off, and a viscous, tan liquid remained. This residue was stirred at 105-108°C for 4.0 hours. Heat was then increased to 290°C, and in 0.5 hours, the mixture became very viscous. The product was 5.92 g of tan, tacky material with some elastic properties.

A small amount of the tan, tacky polymer in a 10-ml Teflon beaker was placed in an oven at 175°C for 3.25 hr and it was converted to a tacky solid which cooled to a malleable disc that could be stretched to about four times its diameter without breaking, provided it was not stretched suddenly. The disc was returned to an oven at 300°C for 15 minutes. While at 300°C, it was a dark brown liquid; after cooling, it was an elastic solid which could be stretched to a transparent film without tearing. The stretched film returned to its original shape slowly. This elastomer was brittle at the temperature of dry ice.

Another disc was formed by heating the tan, tacky polymer in a Teflon beaker for 2.0 hr at 175°C. The product was a clear yellow-orange solid, which was tacky at 175°C but cooled to a non-tacky elastic solid. A 10% solution of this product in benzene was dried on an aluminum panel and the panel was heated then at 125°C for 1.5 hr and at 400°C for 5.0 hours. A smooth coating formed that was unaffected by 19% hydrochloric acid even after being bent. A similar panel heated at 500°C for 1.0 hr yielded a smooth coating that was unaffected by 19% hydrochloric acid except where the panel had been bent. Another panel heated at 400°C for 18 hr also yielded a coating which was clear and unaffected by the acid except where it had been bent. Panels prepared at room temperature, 125°C, and 175°C were not adequately cured.

An attempt was made to cross-link the tan, tacky polymer with benzoyl peroxide. The polymer, 0.6 g, was placed in a 10-ml Teflon beaker, and 0.07 g of benzoyl peroxide was added. The mixture was heated at 125°C for 1.5 hour and at 175°C for 5.5 hours. At 175°C, the product was a dark brown liquid; on cooling, it formed a solid that could be pulled into a film. After being heated further at 125°C for 16 hours, the polymer was still fluid; on recooling, it was elastomeric. A small piece was pulled slowly into a thin 2.5-foot strip without breaking.

b. Reaction of hexaphenylcyclotrisilazane and ethylene glycol without triethylamine

In a 100-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 15.0 g (0.0252 mole) of hexaphenylcyclotrisilazane and 4.17 ml (4.68 g, 0.0756 mole) of ethylene glycol. Heat was applied, and in 0.75 hour the temperature reached 225°C, the reactants formed a homogeneous melt, and a strong odor of ammonia was detected. The mixture was stirred at 185-195°C for 1.5 hour. Then the temperature was increased gradually, and after 1.5 hour the melt was very viscous at 320°C. On being cooled, the product was clear, tan, tacky, and elastic; it weighed 17.98 g. The elemental composition was:

Found: C, 68.50%; H, 5.89%; N, less than 1%

Calculated for $(-\text{Si}(\text{Ph})_2-\text{OCH}_2\text{CH}_2\text{O})_n$: C, 69.38%; H, 5.82%;
O, 13.21%; Si, 11.59%

A small amount of this tacky, elastic product exposed to 23 million roentgens of gamma radiation became even stickier. Another sample of this product that had been heated at 175°C until it became solid (about 4 hours) seemed unaffected by exposure to 10 million roentgens of gamma radiation.

2. Reaction of methylphenyl silylamines with p, p'-biphenol

a. Reaction of methylphenyl methylamino silazane with p, p'-biphenol

Methylphenyl methylamino silazane was prepared by the reaction of methylphenyldichlorosilane with methylamine as described in Report 35, page 18. The purest distilled fraction was probably largely bis-(methylamino)methylphenylsilane with some of the corresponding cyclic compounds. It was treated with p, p'-biphenol in the following manner: In a 100-ml, 3-neck flask equipped with dropping funnel, reflux condenser, thermometer, and magnetic stirrer were placed 3.4 g [0.0187 mole, if the compound had been pure bis(methylamino)methylphenylsilane] and 20 ml of tetrahydrofuran. To this, through the dropping funnel, was added 3.5 g (0.0187 mole) of recrystallized p, p'-biphenol dissolved in 30 ml of tetrahydrofuran. The mixture was refluxed for 2 hours, and the solvent was distilled. The reaction temperature was raised to 250°C for 2 hours and then to 290°C for 1 hour. The product was a viscous, tan liquid at 290°C, and it was rigid and tough at room temperature. When placed in boiling water it became flexible and elastic with slow recovery time. By light scattering in tetrahydrofuran, it was found to have a molecular weight of 150,000. A piece of the polymer was heated with Viton A at 425°C. After 25 minutes it had swelled and split open and was friable when pressed with a spatula. Viton A had cracked on the surface, but it retained a small amount of resilience.

The polymer with a molecular weight of 150,000 was heated at 300°C for 4 hours, and then a small piece was dissolved in tetrahydrofuran to form a gel. The gel was spread on the end of a 0.25-inch wide aluminum strip and then another strip was clamped to it to form a lap joint with an overlap of 0.067 sq in. The joint was heated at 300°C for 30 minutes. The joined strips were subjected to a shear test, and the joint broke at 300 pounds. Thus the shear strength was 4800 psi. On stainless steel strips the value was 4600 psi.

A small piece of the polymer (molecular weight 150,000) was heated at 300°C for 2 hours and then pressed between Teflon sheets in a compression mold at 800 psi and 135°C. A flexible sheet 2-mils thick was formed, but it broke when creased sharply.

b. Reaction of methylphenyl anilino silazane with p, p'-biphenol

The methylphenyl anilino silazane was prepared by the reaction of methylphenyldichlorosilane with aniline as described in Report 35, page 19. The reaction product was distilled and recrystallized as described, and NMR spectra showed the final product to be mainly dianilinomethylphenylsilane.

The recrystallized material, 4.75 g (0.0156 mole), was placed in a 50 ml, 3-neck flask equipped with a distilling head, thermometer, and magnetic stirrer. Recrystallized p, p'-biphenol, 2.9 g (0.0156 mole), was added, and the mixture was warmed slowly to 230°C and held at that temperature for 2 hours. The pressure was reduced with a water aspirator, and 2.0 g of a clear liquid distilled. As the product in the reaction flask cooled, fibers could be pulled from the melt. The softening temperature was about 110°C, but at room temperature the fibers were flexible enough to permit tying knots. When exposed to 9 million roentgens of gamma radiation, the fibers became brittle.

Attempts to form coatings on aluminum produced smooth brittle films with poor adhesion.

III. ATTEMPTS TO INDUCE REACTIONS BETWEEN ETHOXYSILANES AND AMINOSILANES WITH ALUMINUM ETHOXIDE

A. Discussion

Report 35 described the initial efforts to induce a reaction between aminosilanes and ethoxysilanes. No reactions were detected even when ammonium chloride and diphenyldichlorosilane were tried as catalysts. In the past month aluminum ethoxide was tried as a catalyst, and some reaction occurred with diphenyldiethoxysilane, but no routes to useful products are apparent.

B. Experimental Details

1. Reaction of bis(methylamino)diphenylsilane and dimethyldiethoxysilane with 10% of the equivalent amount of aluminum ethoxide

In a 20-ml, 2-neck, round-bottom flask equipped with a reflux condenser, thermometer, and boiling chip were placed 4.6 ml (5.0 g, 0.0206 mole) of bis(methylamino)diphenylsilane, 3.6 ml (3.04 g, 0.0206 mole) of dimethyldiethoxysilane, and 0.22 g (0.0013 mole) of aluminum ethoxide. Heat was applied, and a homogeneous solution formed in 30 minutes when the temperature reached 135°C. After 5.75 hours of heating, the temperature had risen to 160°C, but there was no visible evidence that any reaction had occurred. Heating was continued for a total of 18.25 hours, the final temperature being 188°C. There was no change in appearance or viscosity of the solution. About 2.0 ml (1.82 g) of liquid was distilled at 135°C. Evidently, little or no reaction occurred.

2. Reaction of bis(methylamino)diphenylsilane and diphenylethoxysilane with 10% of the equivalent amount of aluminum ethoxide

In a 25-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser were placed 4.6 ml (5.0 g, 0.0206 mole) of bis(methylamino)diphenylsilane, 5.4 ml (5.61 g, 0.0206 mole) of diphenyldiethoxysilane, and 0.22 g (0.0013 mole) of aluminum ethoxide. Heat was applied, and a homogeneous solution formed when the temperature reached 145°C. About 10 minutes later, at 190°C, the solution began to turn gray. Refluxing began at 299°C, and after 1.25 hour of heating the condensate began to smoke and sputter as it dripped back into the reaction mixture. The vapors were swept out periodically with a stream of nitrogen. Heating was continued, and after 5.75 hours, with the temperature at 360°C, the solution was a dark gray liquid. The product, after cooling overnight, was a gray, tacky, transparent, vitreous solid. An attempt was made to distill off any volatile components in the product. Gentle bubbling began at 60°C at 0.014 mm pressure, but no liquid condensate was obtained even when the temperature was increased to 183°C. The final product was 5.67 g of hard, brittle, transparent gray solid that melted at 75-84°C. It was applied to an aluminum panel from a benzene solution; after curing, it formed a brittle coating that could be scraped from the panel with a fingernail.

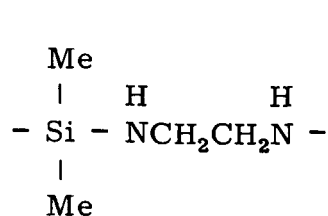
A similar reaction was run with the same amounts of material but without the aluminum ethoxide. After 13.25 hours of refluxing at 315-322°C, the product was 9.48 g of a mixture of white solid and grayish-tan liquid. Evidently the aluminum ethoxide was necessary to obtain the polymer.

IV. REACTIONS OF ETHYLENEDIAMINE SILAZANE

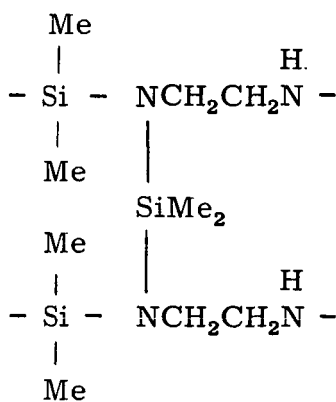
A. Discussion

Ethylenediamine silazane (EDS) has been used previously in this research program to form resilient polymers with good thermal and chemical stability, but they had poor strength. Attempts have been made at various times to improve the strength, but no significant improvement has been accomplished. In the same period, EDS has been blended with other materials to improve their flexibility and thus impart better properties for coatings and resilient plastics. Attempts are now being made to improve EDS by treating it with epoxy compounds and bis(methylamino)diphenylsilane. The reactions have resulted in slight improvements in the ability of EDS to form coatings, but none of the new coatings made from EDS are as tough as those made from other silylamines.

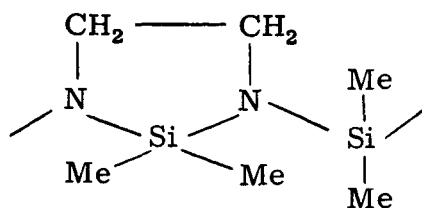
The term "ethylenediamine silazane" was adopted early in the research program for want of a better term. Another appropriate name might have been called the "dimethylsilyl derivative of ethylenediamine." The polymer probably contains a variety of structures; four possibilities are these:



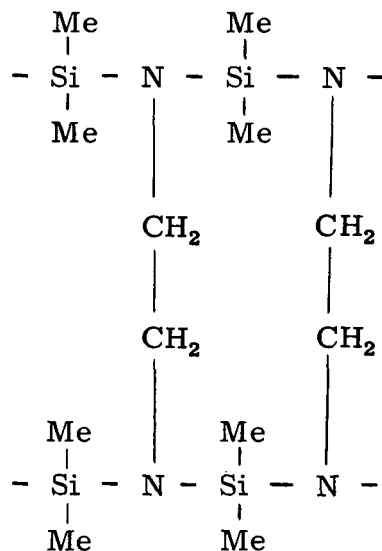
linear form



cross-linked linear form



cyclic form



ladder form

The linear and the cross-linked linear forms offer opportunities for additional cross-linking or chain extension, and it was this possibility that led to the attempted reactions with bis(methylamino)diphenylsilane and ethylene oxide.

Some reaction occurred with bis(methylamino)diphenylsilane as indicated by a slight increase in the toughness of coatings made from the product as compared with those made from EDS alone. The improvement was so small that the product could not be considered of value as a coating agent when used alone. However, the modified EDS should be considered for blending with other materials such as the by-product of hexaphenylcyclotrisilazane.

The reaction with ethylene oxide did not result in any apparent improvement in the properties of coatings made from the product.

B. Experimental Details

1. Reaction of ethylenediamine silazane with bis(methylamino)diphenylsilane

The exact amount of replaceable hydrogen in EDS was not known, and so an empirical method of calculating equivalence based on silicon was adopted. The approximate amount of silicon in EDS was known by analysis,¹ and the amount of silicon in bis(methylamino)diphenylsilane was known from its formula.

a. Reaction with 25% of the equivalent quantity of bis(methylamino)diphenylsilane

EDS was made by the reaction of dimethyldichlorosilane with ethylenediamine as purchased from Union Carbide Chemicals Company.¹ EDS, 5.14 g (0.054 g atoms of silicon), and bis(methylamino)diphenylsilane, 4.31 g (0.014 g atoms of silicon), were stirred and heated together at 250°C for 8 hours in a flask fitted with a thermometer, a reflux condenser, and a drying tube. A gas was evolved that smelled like an amine, and the color of the reaction mixture darkened slightly, but no visible change in viscosity occurred. The product was a light brown, viscous liquid. When the product (dissolved in benzene) was applied to an aluminum panel and heated at 190°C for 5 hours, it formed a fairly tough coating but it could be scratched with a fingernail. It appeared to be slightly tougher and showed less tendency to wrinkle in the thick portions than a coating made with the original EDS.

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1. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, page 85, paragraph 1, and analysis, p. 81, column 1.

b. Reaction with 7% of the equivalent quantity of bis(methylamino)diphenylsilane

EDS, 10.4 g (0.125 g atoms of silicon) and bis(methylamino)-diphenylsilane, 2.17 g (0.009 g atoms of silicon) were stirred and heated together at 250°C for 8 hours in a 25-ml flask fitted with a reflux condenser and drying tube. Amine was evolved, and the color darkened. The product was a dark brown, viscous liquid, and coatings made from it were essentially the same as those described in the preceding reaction.

2. Reaction of ethylenediamine silazane with ethylene oxide

EDS, 11.6 g (0.122 g atoms of silicon), was dissolved in 100 g of anhydrous benzene in a 200-ml, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser. The solution was cooled to 7°C in an ice bath, and liquid ethylene oxide, 0.48 g (0.011 mole), was added. The solution was stirred at 7°C for 30 minutes, and then it was allowed to warm to room temperature over a period of an hour. The solution was refluxed at 78°C for 2 hours, and then the benzene was distilled off. The product, 11.9 g, was a brownish-yellow, viscous liquid. Coatings made with the product were essentially the same as those made with EDS.

Another reaction was tried with gaseous ethylene oxide. EDS, 11.7 g, was dissolved in 50 ml of anhydrous benzene, and the vapor from 60 ml of liquid ethylene oxide was passed over the surface of the benzene solution as it was being stirred. The temperature rose from 24°C to 35°C in 10 minutes and then fell gradually back to 27°C. The reaction mixture was stirred for 4 hours as the ethylene oxide was being added, and then it was refluxed for 4.5 hours. During refluxing, the temperature of the solution was 29°C indicating that an excess of ethylene oxide was present. After the solution had stood at room temperature for 3 days, it was refluxed for 5 hours, during which time the temperature rose to 79°C. At the end of this period the benzene was distilled off. The product was a brownish-yellow viscous liquid that weighed 10.3 g. Coatings made with the product were soft and could be scratched easily. They appeared to be essentially the same as those made with EDS.

V. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

A. Discussion

The study of silicon-nitrogen polymers with phenylene bridges presently involves attempts to purify the starting material, 1,4-bis-(dimethylchlorosilyl)benzene. The first polymer made by the reaction of that compound with methylamine was tougher and more stable than any made since, although all have been fairly similar. Efforts to purify the starting material have not improved the polymer—instead the results seem to indicate that purification has been detrimental.

The most recent preparation of 1,4-bis(dimethylchlorosilyl)-benzene from *p*-dibromobenzene was refined by distillation and by zone refining. The purified material had a neutral equivalent after hydrolysis of 137 (theory, 131). Reaction with methylamine produced a liquid that was less viscous than the first compound made by this reaction (Report 32, page 24). When this most recent preparation was heated in air at 250°C for 16 hours, the product was elastic, wrinkled, and easily torn. The most recent preparation was the fourth started with *p*-dibromobenzene. The second and third preparations were intermediate in strength and tendency to wrinkle.

A polymer made by the reaction of 1,4-bis(dimethylchlorosilyl)-benzene with ammonia was described in Report 35, page 4, paragraph 3. A coating made by curing this material on aluminum for 30 minutes at 350°C was tough and flexible, but attempts to cure it at 350°C and 400°C with 10% by weight of aluminum powder or titanium dioxide were not successful.

Both the ammonia and methylamine derivatives were exposed to gamma radiation to determine whether they were affected significantly. Neither was changed appreciably, except that they both darkened, when they were exposed to 27.7 million roentgens of gamma radiation. The methylamine derivatives appeared to crystallize more slowly after it had been exposed to 13.4 million roentgens and heated to 300°C for an hour.

For comparison Teflon and Viton A were irradiated also. Teflon became brittle after exposure to 9 million roentgens. Viton A lost its cohesion at the surface after being exposed to 13.4 million roentgens and being held at 300°C for an hour, but the main mass was intact and flexible even after exposure to 27 million roentgens.

The liquid methylamine prepolymers (preparations 2, 3, and 4 below) were also exposed to 27 million roentgens of gamma radiation. They became slightly more viscous, and they solidified on being heated at 250°C for 45 minutes, whereas the unirradiated liquids required 16 hours of heating before they became solid at this temperature. The solids produced after irradiation appeared to be slightly stronger, but a precise comparison was not made.

B. Experimental Details

1. Polymers from 1,4-bis(dimethylchlorosilyl)benzene and methylamine

The first preparation of 1,4-bis(dimethylchlorosilyl)benzene was described in Report 32, page 23. After the initial distillation, the main fraction was redistilled, and a fraction with b. p. 98°C at 0.4 mm was obtained. This fraction had a neutral equivalent of 150 (theory, 131.7). The neutral equivalent was determined by weighing a small sample into a glass-stoppered vial, opening the vial under alcohol, and titrating with standard alkali. This fraction was further purified in a Fisher Zone Refiner, Model 341 A. After 12 cycles the product had a neutral equivalent of 137. The purified 1,4-bis(dimethylchlorosilyl)benzene, 28.5 g (0.112 mole), was treated with methylamine as described in Report 32, page 24. The product was a pale yellow oil, 23.5 g (83% of theory), that was lighter in color and less viscous than the product described in Report 32, page 24.

The pale yellow oil was poured into a Teflon mold to a depth of about 2 mm and cured at 250°C for 16 hours. The resulting solid was wrinkled, and it could be torn easily. It was initially elastic, but it crystallized and became flexible but inelastic in about 3 hours at room temperature. When it was held at 400°C for 15 minutes and then cooled, it became considerably weaker.

The polymer just described was the fourth preparation made with p-dibromobenzene. The second and third were intermediate between the first and fourth in viscosity of the liquid prepolymer and in physical properties of the polymers. Nuclear magnetic resonance spectra indicated that the degrees of polymerization were higher in the earlier preparations. We are not sure of the validity of this deduction, but it should not be overlooked. As shown in Table I the number of N-methyl groups decreases with relation to phenyl protons and with relation to Si-methyl plus NH protons as the degree of polymerization increases. Table I shows that the fourth preparation had the lowest degree of polymerization if this method is reliable; and, surprisingly, it suggests that the degree of polymerization changed in 24 hours.

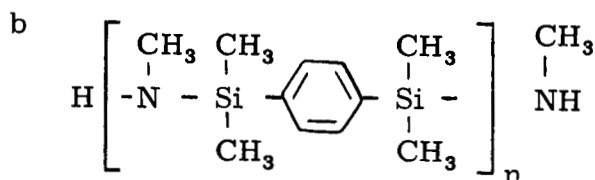
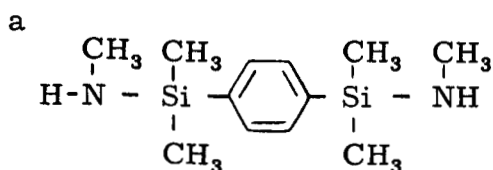
Experiments to study the effects of radiation were done with gamma radiation from cobalt-60 at a rate of 1.4×10^5 roentgens per hour. The liquid prepolymers appeared to polymerize faster after exposure to 27 million roentgens. They became solid in 45 minutes at 250°C, whereas 16 hours would have been required without irradiation. The solid methylamine polymer (Report 32, page 25) was exposed to 13.4 million roentgens, and it appeared unchanged except that it was slightly darker. After being heated at 300°C for an hour, it then remained elastic for 8 hours at room temperature, whereas the original polymer would have crystallized in an hour. After the same radiation exposure, Teflon became brittle and Viton A appeared to be unchanged, except that it could be scratched on the surface after it was heated at 300°C for an hour. Further exposure to a total of 27 million roentgens produced no further changes in any of the three compounds.

2. Polymer from 1,4-bis(dimethylchlorosilyl)benzene with ammonia

The reaction of 1,4-bis(dimethylchlorosilyl)benzene with ammonia and the polymerization of the product were described in Report 35, page 4, paragraph 1. The white, waxy, solid polymer was dissolved in benzene to form a 10% solution, 1% by weight of aluminum powder was stirred into the solution, and the mixture was applied to aluminum panels in thin layers. These did not cure to solid films at 250°C in 16 hours, nor did they cure at 300°C, 350°C, or 400°C in an hour. Similar results were obtained with the white, waxy solid polymer that had been polymerized further by heating in nitrogen as described in Report 35, page 24, paragraph 3. Neither of these polymers was visibly changed by 27 million roentgens of gamma radiation, except for darkening of color.

Table I. Ratios of Substituents in Material Made from Methylamine and 1,4-Bis(dimethylchlorosilyl)benzene

	<u>Phenyl protons</u>	<u>N-Methyl protons</u>	<u>Si-Methyl protons + NH protons</u>
Monomer ^a			
theory	4	6	14
Polymer ^b			
theory, n - 1	4	6	14
theory, n - 2	8	9	26
theory, n - 3	12	12	38
theory, n - 4	16	15	50
theory, n - 5	20	18	62
theory, n - 6	24	21	74
found, second preparation	4	3.4	12.2
or	20	17	61
or	24	20.4	73.2
found, third preparation	4	3.5	12.7
or	20	17.5	63.5
or	24	21	76.2
found, fourth preparation	4	4.6	10.7
or	8	9.2	21.4
found, fourth preparation (24 hours later)	4	4.7	13.5
or	8	9.4	27



VI. ANTICIPATED WORK

The following work is planned for the next two months:

The reactions of alkali derivatives of silylamines with ethoxysilanes and organo-metallic compounds such as aluminum ethoxide will be studied.

The work on silicon-nitrogen polymers with phenylene bridges in the main chain will be continued in an effort to understand why the most recently prepared polymer was weaker than its predecessors. Thermal polymerization before curing will be tried.

Heats of combustion will be studied as indicators of aromaticity in cyclic silazanes.

Methods of silylating polyethylenimine will be studied. If such a reaction can be accomplished, it will produce a silicon-nitrogen polymer with high molecular weight.

Work will be continued on the reaction of silicon-nitrogen compounds with difunctional hydroxyaromatic compounds because these have shown physical properties.

Reactions and possible cross-linking of ethylenediamine silazane with epoxy prepolymers will be attempted to improve the molecular weights and physical properties.

The reactions of silicon tetrafluoride with silylamines and polyethylenimine will be studied. In the previous year's study, silicon tetrafluoride and hexamethylcyclotrisilazane reacted, and the product was heated to form an exceptionally stable compound that was not investigated in detail.

Attempts will be made to form a polymer by the reaction of phthalocyanino-dichlorosilane with ammonia.

Work is also planned to study methylhydrogen silazanes as polymers that can be cured at low temperatures and to study polymers of methyltrichlorosilane and silicon tetrachloride.

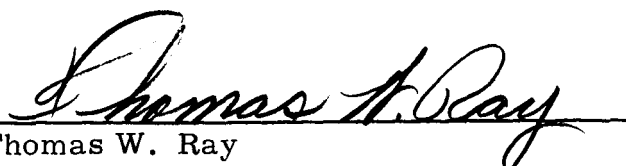
VII. TIME EXPENDITURE

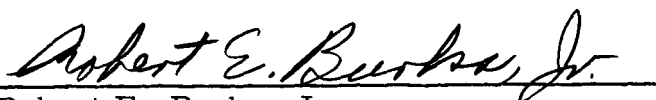
The time expenditure during the monthly period covered by this report (January) was 967.5 man-hours.

ACKNOWLEDGMENTS


Mr. Robert E. Lacey, Senior Chemical Engineer, has assisted with the planning and interpretation of the laboratory work. Miss Mary Ann Fromhold, Assistant Chemist, and Mr. Charles L. Christy, Jr., Chemical Technician, assisted with the laboratory work.

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Physical Sciences Research

Birmingham, Alabama
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PROGRAM PLANNING CHART

	Allotted time, man-hours	1963												1964		
		April	May	June	July	August	September	October	November	December	January	February	March			
A. Synthesis of Polymers and Compounds with Desired Characteristics																
1. Lubricants - unsymmetrical derivatives of cyclic silazanes (see B. 1. b)	400				X											
2. Elastomers - silyl derivatives of ethylenediamine (see B. 7)	400				X											
3. Structural plastics	900	X	X	X	X	X										
B. Study of the Chemistry of Silicon-Nitrogen Compounds																
1. Metallation of silylamines as a method of synthesis	500	X	X	X	X	X										
a. Polymers	-															
b. Lubricants (see A. 1)	900						X	X	X	X	X	X	X			
c. Organometallics																
2. Polymerization of cyclic silazanes at high temperatures and pressures	280				X											
3. Condensation polymerization of silylamines with difunctional aromatic compounds	280						X	X	X	X	X	X	X			
4. Steric factors to inhibit cyclization	900						X	X	X	X	X	X	X			
5. Polyethylenimine as a source of silicon-nitrogen polymers	400						X	X	X	X	X	X	X			
6. Properties of methyldiimine silazanes	200															
7. Elastomers from ethylenediamine silazanes (see A. 2)	-															
8. Addition of silicon tetrafluoride to silazanes and amines	280															
9. Heats of combustion as indicators of aromaticity	420															
10. Polymers from methyldichlorosilane and silicon tetrachloride	420															
11. Silicon-nitrogen compounds with aromatic bridges	510	X	X	X	X	X	X	X	X	X	X	X	X			
12. Factors affecting hydrolytic and thermal stabilities	510															
C. Evaluation of Polymers (thermal, hydrolytic, and radiation stability)	510															
D. Applications - Search for New Uses	510															
E. Heat Barriers	510															
F. Preparation of Final Report	170															
	9000															

Descriptions correspond to sections of Proposal 2186 - March 20, 1963.